

PTO 06-6861

CY=EP DATE=19931208 KIND=A1  
PN=0 573 348

METHOD OF DEPOSITING METAL ON A SUBSTRATE AND DEVICE FOR ITS  
IMPLEMENTATION  
[PROCEDE DE DEPOT DE METAL SUR UN SUBSTRAT ET DISPOSITIF POUR SA MISE  
EN OEUVRE]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. SEPTEMBER 2006

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10):	<i>Europe</i> <del>France</del>
DOCUMENT NUMBER	(11):	0 573 348
DOCUMENT KIND	(12):	A1
PUBLICATION DATE	(43):	19931208
PUBLICATION DATE	(45):	
APPLICATION NUMBER	(21):	93401398.8
APPLICATION DATE	(22):	19930602
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	C 23 C 16/14; C 23 C 16/44
DOMESTIC CLASSIFICATION	(52):	
PRIORITY COUNTRY	(33):	FR
PRIORITY NUMBER	(31):	9206706
PRIORITY DATE	(32):	19920603
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
PRIORITY DATE	(32):	
DESIGNATED CONTRACTING STATES	(84):	
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TITLE	(54):	METHOD OF DEPOSITING A METAL ON A SUBSTRATE AND DEVICE FOR ITS IMPLEMENTATION
FOREIGN TITLE	(54):	PROCEDE DE DEPOT DE METAL SUR UN SUBSTRAT ET DISPOSITIF POUR SA MISE EN OEUVRE

The present invention pertains to a method depositing in the /2\* vapor phase a metal (such as copper, tungsten, titanium, tantalum, molybdenum) on a substrate, as well as a device for the implementation of this method.

The method of chemical deposition of metal in the vapor phase (CVD) is widely used to produce thin layers of metal, of good quality; this method has been applied in many industries and especially in the electronics industry.

In the latter industry deposits of aluminum, chromium, copper, silver, gold or nickel, and so forth are, indeed, used particularly in the production of complex or hybrid electronic circuits, starting with several silicon chips assembled on a single substrate of silicon and/or for the production of the interconnection lines.

In a general way these layers are traditionally made under vacuum, by means of thermo-evaporation or even by cathodic spraying; the deposit can be made over the entire surface of the substrate, then engraved, or through a mask so as to obtain directly the desired pattern.

To the extent that it is preferred, in this field, of depositing the metal at temperatures that are quite low, especially to allow one to produce the deposit in the presence of substrates that are temperature sensitive, some CVD techniques adapted to such situations have been described.

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\* Numbers in the margin indicate pagination in the foreign text.

The European patent application EP 297,348, in the name of IBM, describes a method of chemical deposition of copper in the vapor phase (CVD technique), which uses as the starting product or precursor an organometallic complex of the cyclopentadienyl metal kind, in gas form and including a cyclopentadienyl nucleus, a donor ligand of two electrons (trivalent phosphines, amines and arsines) and a metal of the 1B group in oxidation state +1.

The substrate on which the deposit must be applied is heated, in such a way that the reaction of decomposition of the vapors of the precursor complex is accomplished in the area of the said substrate and leads to deposition of the metal (group 1B) in the area of the said substrate.

This reaction, carried out at low temperature, the use of the metal in its oxidation state +1 and the dimerization of the cyclopentadienyl nucleus in a stable and volatile molecule are the essential characteristics that lead to the depositing of metal on a substrate under the conditions described in this application EP 297,348.

Other documents describe the use of other organometallic precursors, such as compounds of the trifluoroacetylacetone or hexafluoroacetylacetonate kind.

The patent US 4,842,891 in the name of Hitachi Ltd. describes a method of forming a layer of copper by CVD, in which the starting product is copper nitrate. The copper nitrate vapor is reduced with

a reducing gas with low molecular weight such as carbon monoxide, hydrogen, methane, ammoniac, such that the metallic copper is precipitated on the surface of the substrate, held at a temperature of 200-650°C. The reaction conditions are more particularly described: the pressure in the reaction chamber must be between 0.1 and 3 torrs and the copper nitrate/reducing gas ratio is greater than the stoichiometric ratio.

However, these CVD techniques present a certain number of disadvantages:

- The deposit is of poor quality and includes in particular some impurities (carbon, oxygen, and so forth); this is particularly the case in the CVD techniques that use as the starting product an organometallic compound, in which the impurities such as carbon or oxygen formed during the decomposition of the organometallic compound, which may, moreover, turn out to be unstable, remain in significant quantities in the metal layer and especially in the copper layer that is produced;
- And/or the reaction temperatures are excessive;
- And/or the deposition rate, on the order of 0.1-0.5 micrometer/h is too slow.

Such techniques are therefore are not very easy to achieve in industrial applications.

The first CVD techniques described made use of  $\text{CuCl}_2$  (oxidation state +2) at temperatures between 400 and 1200°C and had the disadvantage of have excessively high reaction temperatures.

The article in the name of C. Lampe-Onnerud et al, which appeared in J. Physique IV ( $\text{C}_2$  Colloquium), Suppl. J. Physique II, 1991, 1, 881-888, describes a method of chemical deposition of copper in the vapor phase, which uses as the precursor some  $\text{CuCl}$ ; the authors of this article have shown that in order to obtain a deposit of copper on a substrate, the evaporation of the  $\text{CuCl}$  from a solid product such as a powder is a critical step of the method.

Under the conditions described in this article the  $\text{CuCl}$  was evaporated at a temperature between 300 and 350°C and the deposition temperatures were between 350 and 500°C.

The variations in the evaporation rate are essentially due to two factors: deviation of the equilibrium during evaporation and formation of a hydroxychloride on the surface of the solid product; the authors of this article have concluded that a reproducible deposition from  $\text{CuCl}$  could be obtained only by means of appropriate treatment of the solid product.

In addition, they studied more particularly two substrates:  $\text{SiO}_2$  and  $\text{Si(III)}$ .

Some deposits of copper, on a substrate of  $\text{SiO}_2$  (evaporation temperature: 350°C; deposition temperature: 500°C; partial pressure /3

of CuCl: 1.2 Pa, in the presence of hydrogen as the reducing gas), with an average thickness of 1.5 micrometers, were deposited in 5 hours, which corresponds to a deposition rate of about 0.3 micrometers/h.

Under the conditions described in this article some chlorine is detected on the surface of the deposited copper particles; moreover, in the case when the substrate is Si(III), one observes a certain instability of the deposit.

The method discussed in this article has the disadvantage of leading to a deposit of poor quality (impurities), at too slow a rate (0.3 micrometer/h) for industrial applications.

It is also apparent from this document that the main difficulty in the implementation of inorganic precursors such as CuCl is due to the low vapor tension of the latter at ambient temperature, and therefore the difficulty of obtaining a concentration in the vapor phase that is sufficiently great to lead to depositions speeds of a few micrometers per minute.

This shows that the sublimation sources of copper halogenides, starting from the solid phase, are generally not very satisfactory because the variations of surface properties of the solid, in the course of sublimation, lead to significant variations of sublimation speed and therefore to a variation of the gaseous halogenide flow rates.

The present invention consequently has the goal to be able to provide a method of metal deposition by means of CVD, which better meets the needs of practice than the currently used methods, by allowing one to obtain a deposition speed of a few micrometers per minute, under conditions of pressure and temperature that are particularly well adapted to the substrates to be treated and which allow homogeneous or selective deposition of a good quality layer of metal.

One aim of the present invention is a method of vapor phase metal deposition, on a substrate, by reduction of a halogenide of the said metal in the gas state, characterized in that it includes:

(a) The production of the said metallic halogenide, in situ, based on a means of production included in a reaction chamber that contains the substrate, by placing in contact a gaseous halogen with a metal solid brought to a temperature between 500°C and 700°C, and;

(b) The reduction, in the said reaction chamber held at a total pressure between 13.3 and 133.3 pascals (0.1 and 1 torr), of the said gaseous metallic halogenide produced in the course of stage (a) and whose partial pressure is between 1.33 and 133.3 pascals (0.01 and 0.1 torr), in the presence of at least one reducing gas, which gas has a partial pressure on the order of that of the metallic halogenide, in order to obtain a deposit of pure metal, at a rate on the order of micrometers per minute, on the said substrate brought to a temperature between 200°C and 400°C.



According to one advantageous mode of implementation of the said method the metal is chosen from among copper, tungsten, titanium, tantalum and molybdenum.

According to another advantageous mode of implementation of the said method the reducing gas is chosen in the group that includes hydrogen,  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_8$ ,  $\text{Si}_3\text{H}_8$ ,  $\text{SiH}_2\text{Cl}_2$ ,  $\text{SiHCl}_3$ , and  $\text{SiH}_3\text{Cl}$ .

According to another advantageous mode of implementation of the said method the substrate is chosen in the group that includes semiconductor substrates, especially those based on silicon and substrates made of plastic.

Based on the structure of the substrate the deposit can be homogeneous or selective.

According to one advantageous arrangement of this mode of implementation, when the surface of the substrate is homogeneous in nature, silicon or metal, one will obtain a deposit in a homogeneous layer on the order of micrometers per minute.

According to another advantageous arrangement of the said mode of implementation, when the surface of the substrate has some structures of different natures (that is, areas of raw silicon and areas of silicon oxide), the said metal layer is deposited selectively only in the area of certain zones, silicon or metal.

For example, by locally changing the nature of the surface of a substrate made of silicon oxidized by a series of stages of photolithography and engraving that form especially lines of bare

silicon, one will observe a deposit of metal (especially copper), only in the zones of bare silicon while the metal is not deposited in the zones of oxidized silicon. Such selectivity is also seen with substrates in which one part of the surface is oxidized, the remainder of the surface being covered by a metal, copper or chromium for example.

The same is true of substrates that have some zones of copper and some zones of organic insulator; in this case one will get a metal deposit without the dielectric having traces of metallic deposition.

Such a method is particularly advantageous in the metal coating of the last levels of interconnection of integrated circuits, in the making of interconnection networks for hybrid circuits, as well as in the metal coating of plastics.

According to another advantageous mode of implementation of the said method the reaction gases (halogen and/or reducing gas) are combined with a neutral carrier gas.

The presence of this carrier gas, which advantageously can be argon, assures the transport of the reaction gases and prevents a homogeneous phase reaction; its partial pressure represents advantageously about 80% of the total pressure.

Another goal of the present invention is a device for putting the said method into operation, the kind that includes a reaction chamber that includes a substrate, some means of heating the said

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substrate and at least one source of reducing gas, characterized in that the said reaction chamber also includes a means of production in situ of a gaseous metal halogenide, which includes at least in combination:

- A source of gaseous halogen, combined with some devices for regulating the entry flow rate of the said halogen;
- A support (or cupel) that contains a metal in solid form;
- Some means of homogenizing the output flow of the gaseous metallic halogenide that is formed toward the substrate; and
- Some means of heating and regulating its temperature.

Advantageously the regulation of the gas flow rates is assured by some large-scale flow rate meters.

According to one advantageous mode of implementation of the said device, the said means of producing gaseous metallic halogenide surrounds the said substrate and allows uniform radial injection of the halogenide on the substrate.

According to another mode of advantageous implementation of the said device, the said means of producing gaseous metallic halogenide also includes a source of a carrier gas.

Advantageously, such a device allows one to produce, in the case of copper for example, a source of gaseous  $\text{CuCl}$  with adjustable flow rate, because under the temperature and pressure conditions as defined in the method in conformity with the invention the kinetics of formation of the  $\text{CuCl}$ , starting with  $\text{Cl}_2$  gaseous chlorine and solid

copper, is defined and controllable; indeed, such a device, which allows radial and therefore uniform injection of the copper halogenide, leads to one obtaining a concentration in the vapor phase that is sufficiently great to obtain metal deposition rates on the order of one micrometer per minute.

In addition to the preceding arrangements, the invention also includes other arrangements, which will be apparent from the following description, which refers to examples of implementation of the method in conformity with the invention and with a detailed description of the device of the invention, with reference to the attached drawings in which:

- Figures 1 and 2 represent one mode of implementation of the device in conformity with the invention, in longitudinal cross section, in which the means of producing metallic halogenide in situ (copper in the representation given here) surrounds the substrate (annular shape).

It should be understood, however, that these drawings and the corresponding descriptive parts, as well as the examples, are given solely as an illustration of the aim of the invention, of which they do not in any way constitute a limitation.

Figure 1 presents a device in conformity with the invention, in longitudinal section, which includes advantageously a reaction chamber 10, including both a means of producing gaseous copper halogenide 11 and a deposition zone of copper 12 on a substrate 30.

The means of producing gaseous copper halogenide 11 includes in the execution presented in Figures 1 and 2:

- A ring-shaped cupel (or support 20) closed by a perforated base 25, in which a metal 26 can be housed, especially copper in solid form. Some heating and temperature regulating devices 21 are combined with the cupel 20, which allow the heating of the assembly of the halogenide production device, these means allowing one to bring the temperature of the copper to about 650°C; in the implementation shown these heating and temperature regulating devices 21 are represented by a resistor and can be made of a series of thermal cables embedded in the wall of the production device and temperature regulated by an electric power control dispersed in the resistors;
- Gaseous chlorine is then sent through pipe 22, which drains outside the production device 11, below the perforated base 25 of the cupel 20, on the heated solid copper 26; the flow of the said halogen is homogenized by a series of baffle plates not shown in Figures 1 and 2; in the implementation shown in the said Figures 1 and 2, the pipe 22 also transports the carrier gas, which can be argon in particular;
- Above the cupel 20 a deflector plate 24 is arranged, as shown in Figure 2, in the form of a ring-shaped plate, which returns the metallic halogenide vapors formed toward the X-X axis (Figure 2) of the reaction chamber and toward the substrate 30; and

- The walls 110 of the reaction chamber 10 are combined with a heating and temperature regulating device, which allows one to maintain the temperature of these walls at about 250°C in order to prevent CuCl deposits on the latter.

This gaseous copper halogenide production means 11 allows injection of the said halogenide into the reaction chamber per se, in its X-X central part, also held at a temperature of about 250°C.

In the execution shown in Figures 1 and 2 the flow rate of the gaseous CuCl is controlled by the flow rate of the chlorine sent into the device 11.

The CuCl produced is found in the vicinity of the substrate 30 and is placed in contact with a reducing gas or a mixture of reducing gases, sent into the reaction chamber 10 via the intermediary of 5 pipe 23, which opens from the exterior of the said reaction chamber 10, immediately above the substrate 30; the input flow rates of the said reducing gases are regulated by the help of specific flow rate meters.

The reduction of the gaseous metallic halogenide to a solid metal is then carried out in the copper deposition zone 12, which advantageously includes, in the execution shown in Figure 1:

- A substrate 30, combined with some heating devices 34, which in this mode of implementation are represented, in a non-limiting way, by a halogen bulb located to the rear of a quartz porthole 35, combined with a layer of helium 36, located beneath the

substrate 30 (silicon plate, for example), so as to homogenize the temperature of the said substrate; on the substrate 30 there will be formed, under the conditions defined in the method in conformity with the invention, a layer of pure metal (copper in the implementation shown here), at a rate on the order of micrometers/min; the said substrate 30 is carried by a support 32, which can be displaced along a vertical shaft, so as to regulate the distance between the source of metallic halogenide production and the substrate, so that it will be on the order of centimeters;

- Some pumping devices 31 of the volatile compounds formed during the reduction reaction of the  $\text{CuCl}$ ; and
- A detachable wall 33, which allows loading of the reaction chamber 10.

The device in conformity with the invention has the advantage of providing a source of halogenide produced in situ, firmly connected with the reaction chamber.

In an advantageous manner, in the device in conformity with the invention, which includes a means of production in situ of a metallic halogenide in the vicinity of the substrate, regulation of the flow rate of chlorine injected into the said device allows, for temperatures greater than  $350^{\circ}\text{C}$ , precise control of the flow rate of the  $\text{Cu}_3\text{Cl}_3$  that was placed in contact with the substrate and therefore a concentration of the latter in the vapor phase that is sufficiently

large to obtain copper deposition rates on the order of one micrometer per minute.

Also in an advantageous way, the injection of the reactant product ( $\text{CuCl}$ ) in the area of the copper deposition zone 12 is accomplished through a series of orifices, uniformly distributed on the perimeter surrounding the substrate 30 (not shown in Figures 1 and 2), thus assuring communication between the halogenide production device 11 and the deposition zone 12.

EXAMPLE 1: Implementation of the method: depositing of copper on a substrate with heterogeneous zones, in a device such as the one described in Figures 1 and 2.

A substrate that has zones of silicon and zones of silicon oxide allows one, under the conditions defined subsequently, to obtain selectively a deposit of copper on the silicon only.

The copper halogenide is formed in the halogenide production device (ring-shaped), which surrounds the substrate and is located 1-2 cm from the said substrate, by directing some gaseous chlorine over some strips of copper heated between  $500^{\circ}\text{C}$  and  $700^{\circ}\text{C}$ , preferably at  $650^{\circ}\text{C}$ . The walls of the reaction chamber 10 are held at a temperature greater than  $250^{\circ}\text{C}$ , which allows one to limit the recondensations of  $\text{CuCl}$  on these walls. Moreover, the heating of the walls 27 of the cupel 20 of the halogenide production device 11 is important because:



- The CuCl vapor tension is too weak at low temperature to be able to assure transfer in sufficient quantities of CuCl into the solid metal deposition zone;
- It is only above 250°C that the reaction of CuCl formation is complete and allows one to obtain in the reaction chamber some CuCl that is free of residual chlorine; and
- Above 500°C the kinetic aspects of CuCl formation are too slow to be able to lead to adequate flow rates.

The resulting compound ( $\text{Cu}_3\text{Cl}_3$ ), in which the copper is included in an oxidation state +1, reacts in the gaseous phase with a mixture of reducing gases ( $\text{H}_2$  and  $\text{SiH}_4$ ) in contact with the said substrate brought to 350°C, in such a manner that the total pressure in the reaction chamber 10 is 100 pascals, the partial pressure of reducing gases is 1 pascal ( $\text{H}_2$ : 0.8 pascal;  $\text{SiH}_4$ : 0.2 pascal) and the copper halogenide pressure is 1 pascal; one thus obtains a deposit of copper at a rate of 0.5 microns/minute. The measured resistance value is about 2 microohms  $\text{cm}^{-1}$ , a value near that of the monolithic copper. This is particularly due to the absence of solid reactants that could be trapped in the copper as well as to the strong vapor tension of the gaseous reactants eliminated by pumping.

EXAMPLE 2: Depositing of copper on a homogeneous substrate.

- a) One chooses as the substrate a plate of silicon;
- b) The substrate is placed on a heating hearth that allows one to achieve temperatures between 200°C and 400°C;

c) The  $\text{CuCl}$  is formed in one part of the chamber very near the substrate by directing some chlorine over some strips of copper heated between  $500^{\circ}\text{C}$  and  $700^{\circ}\text{C}$ .

The remaining portion of the protocol is identical to that of /6  
Example 1.

The operating conditions discussed in Figures 1 and 2 also apply to the other metals mentioned.

As is evident in the preceding discussion, the invention is not limited only to those of its modes of implementation, of execution and of application that have just been described more explicitly; on the contrary it includes all variants that could come to the mind of the technician of this art, without thereby departing from the scope or the range of the invention.

#### Claims

1. Method of depositing metal in the vapor phase, on a substrate, by reduction of a halogenide of the said metal in the gaseous state, characterized in that it includes:

(a) The production of the said metallic halogenide, in situ, from a production device (11) included in a reaction chamber (10) that contains the substrate, by placing a gaseous halogen in contact with a solid metal brought to a temperature between  $500^{\circ}\text{C}$  and  $700^{\circ}\text{C}$ , and

(b) The reduction, -- in the said reaction chamber held at a total pressure between 13.3 and 133.3 pascals (0.1 and 1 torr) -- of

the said gaseous metallic halogenide produced during step (a) and whose partial pressure is between 1.33 and 13.3 pascals (0.01 and 0.1 torr), in the presence of at least one reducing gas, which gas has a partial pressure on the order of that of the metallic halogenide, in order to obtain a deposit of pure metal, at a rate on the order of micrometers per minute, on the said substrate brought to a temperature between 200°C and 400°C.

2. Method according to Claim 1 characterized in that the metal is chosen among copper, tungsten, titanium, and molybdenum.

3. Method according to Claim 1 or Claim 2 characterized in that the reducing gas is chosen in the group that includes hydrogen,  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$ ,  $\text{Si}_3\text{H}_8$ ,  $\text{SiH}_2\text{Cl}_2$ ,  $\text{SiHCl}_3$ ,  $\text{SiH}_3\text{Cl}$ .

4. Method according to any of the Claims 1 to 3 characterized in that the substrate is chosen in the group that includes semiconductor substrates, especially those with silicon base and plastic substrates.

5. Method according to any of the Claims 1 to 4 characterized in that when the surface of the substrate has a homogeneous nature, silicon or metal, one obtains a deposit in a homogeneous layer on the order of micrometers per minute.

6. Method according to any of the Claims 1 to 4 characterized in that when the surface of the substrate has structures of different kinds, the said metal layer is deposited selectively in the area of certain zones.

7. Method according to any of the Claims 1 to 6 characterized in that the gaseous halogen and/or the reducing gas are combined with a neutral carrier gas.

8. Device for the implementation of the method according to any of the Claims 1 to 7, of the kind that includes a reaction chamber (10) containing a substrate (30), some devices for heating the said substrate (34) and at least one source of reducing gas (23), characterized in that the said reaction chamber includes, in addition, a device (11) for production in situ of a gaseous metal halogenide, which includes at least in combination:

- One source of gaseous halogen (22), combined with some devices for regulating the intake flow rate of the said halogen;
- A support (20) that contains a metal in solid form;
- Some means of homogenization of the outlet flow of the gaseous metallic halogenide formed, toward the substrate; and
- Some devices for heating and regulating its temperature (21).

Which means (11) of gaseous metallic halogenide surrounds the said substrate and allows uniform radial injection of the halogenide onto the substrate.

9. Device according to Claim 8 characterized in that the said device (11) for production of gaseous metallic halogenide includes in addition a source of a carrier gas.

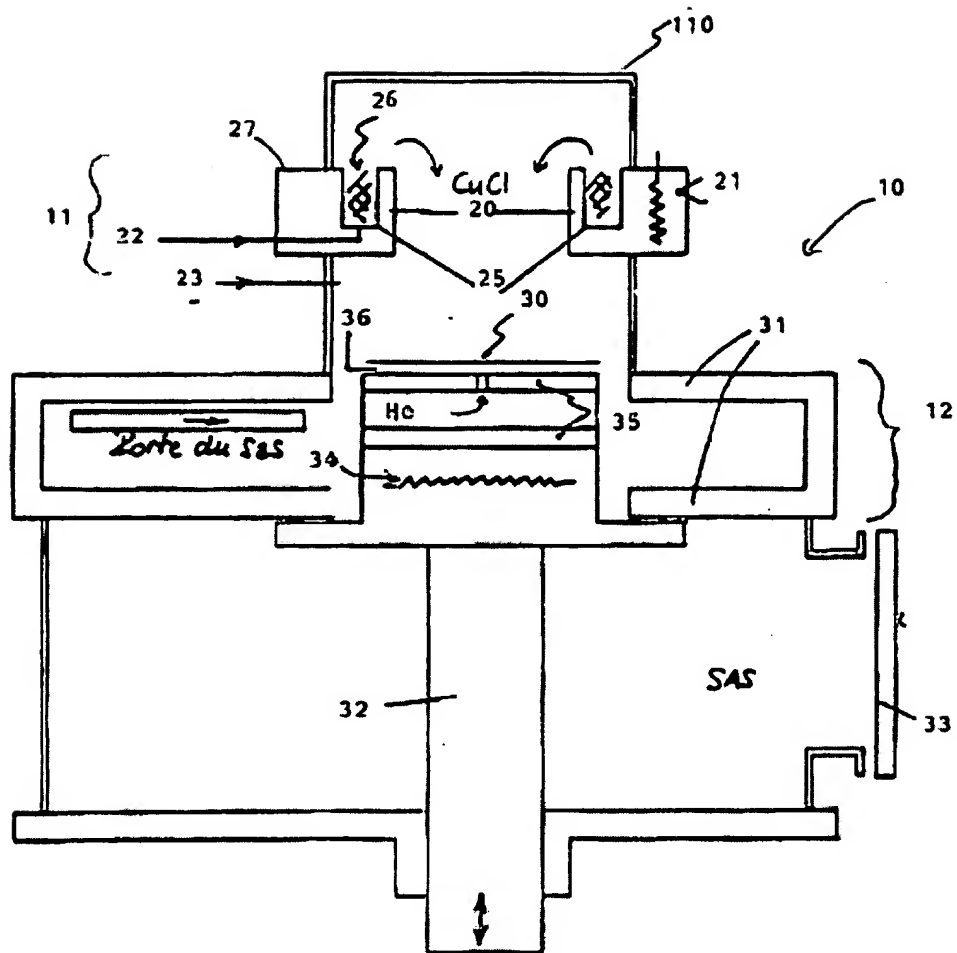


FIGURE 1

Key:

Porte du sas = airlock gate

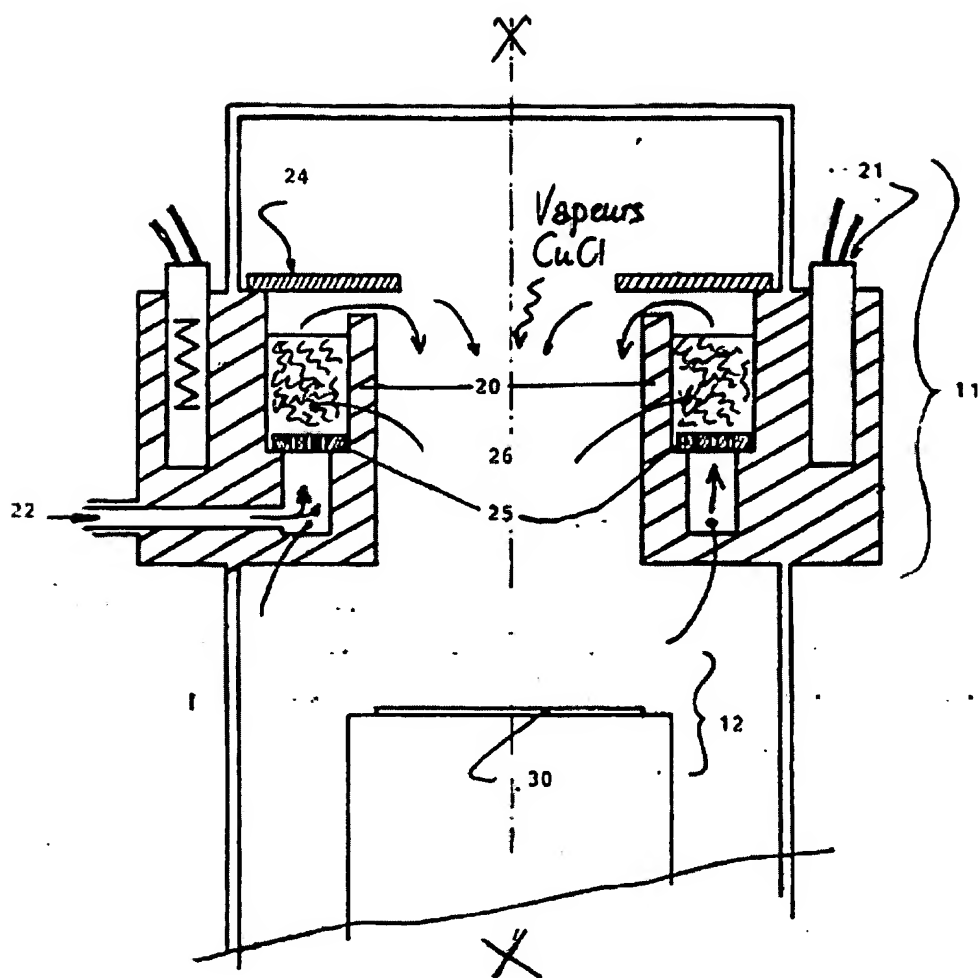


FIGURE 2

Key:

Vapeurs = vapors